Soil Science Division

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CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS OF SOILS OF ARID ZONES

A manual for technical laboratory training

ANALYTICAL TECHNIQUE No. 1

Damascus 1979

THE ARAB CENTER
FOR THE STUDIES OF ARID ZONES AND DRY LANDS
(ACSAD)

THE ARAB CENTER

For The Studies of Arid Zones & Dry Lands

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P. O. Box. 2440 Damascus Syria

Cable : ACSAD - Damascus Phon { 457084 / 457001 / 750401

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CATION EXCHANGE CAPACITY & EXCHAGEABLE CATIONS OF SOILS OF ARID ZONES

- Laboratory Handbook No. 1 -

Jean - Olivier JOB*

THE ARAB CENTER FOR THE STUDIES OF ARID ZONES
AND DRY LANDS

(ACSAD)

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* Senior Chemist, Office de la Recherche Scientifique et Techniaue, Outre-Mer, (ORSTOM) PARIS - FRANCE.

I - Exchangeable Properties of Soils Of Arid Zones.

A. INTRODUCTION

Soils of arid zones are generally little altered and contain non-weathered minerals and varying quantities of soluble salts. Most frequent salts are calcium carbonate, calcium sulfate, sodium chloride, sodium carbonate; when a soil contain sufficient amount of soluble salts its exchange sites may be saturated. Their neighbouroud may contain a high concentration of cations when water dissolves the salt and an equilibrium occurs between dissolved and fixed ions.

It is therefore difficult to investigate what are the true exchange properties of such soils, since any analitycal experiment perturbates this equilibrium. In addition to that, clay minerals, organic matter and more or less amorphous materials, which exchange ions have a behaviour depending on the nature of exchanged ion. Involved factors are size and electric charge among others.

The purpose of this short study is to help the analyst to select, among the nomerous proposed methods those which are suitable for routine analysis. An ample litterature has been devoted to methodology but few procedures, no matter how elegant they are can be used for routine work and large scale analytical programs. None of them is applicable to all kinds of soils, regardless their chemical composition.

B- Exchangeable Cations and Soil Properties:

Different authors have proposed direct linear relationship between C.E.C and soil properties as clay percentage and organic matter (Ollat Combeau 1960, Lové, Helling 1964...) C.E.C has been also related to hygroscopic water (BANIN, AMIEL 1969, RHOADES 1977), specific area of soil (CURTIN, SMILLIE 1976). Therefore clay mineral and organic matter are the first parameters to be considered.

On the other hand, chemical composition of soil may cause technical difficulties. In respect of that, gypsum, calcium carbonate and soluble salts are the other parameters determining the choice of a specific method.

a) clay minerals:

i) Type 1/1 (7 Augstroms)
Kaolinite, halloisite, dickite, nacrite... have a low C.E.C (around 20 meq/100 g of clay) due to a small area of exchange on the external surface of clay layer.

No irreversible fixation of cation is to be feared of and any method could be used, if the soil is not very acid. Though minerals of this family are usually formed under acidic conditions (Caillere, Henin) unusual in arid zones, they can be found far from their original place as the effect of transport and deposition of sediments.

ii) Type 2/I (10 Angstroms)
For montmorillonite and nontronite, the distance between layers is usually too large to allow irreversible fixation of K and Na which may be used as acetate for saturating the complex.

These minerals are formed under alcaline conditions, (especially Mg rich), their specific C.E.C is 100 - 130 meq/100 g. Increasing binding force of cation on fixation sites is: Na - K - Mg - Ca.

For illites, C.E.C is lower (20 - 30 meq/100 g), K and NH_4 may be fixed strongly between two layers in non exchangeable form. Increasing binding force is: Na - Mg - Ca - K/NH_4.

C.E.C of vermicullites, hallite, stevensite is slightly higher (35 - 40 meq/100 gr.)

In consequence salts of Amonium should not be used for the first step of saturation when a sample contain more than 40% of 2/1 clay type, if an accurate determination of exchangeable K is requested.

b) <u>organic matter</u>

Percentage of organic matter is usually less than 2% in arid zones and no specific methodology is required. Nevertheless, organic meterial has a high C.E.C (100 - 200 meq/100 gr.) and different results may be found depending on either organic debris have been removed or not prior to analysis.

c) <u>Chemical Composition</u>

The chemical composition of a soil sample justifies by itself the choice of a specific methodology for EC or C.E.C determinations. The solubility of carbonates and sulfates of Ca and Mg creates problems during the extraction of E.C.

As a general rule it is better to know carbonate, gypsum and soluble salt percentage before attempting to determine EC and CEC; in many cases, calcareous, gypsic and saline soils require a different approach as far as methodology of EC is concerned.

- CHAPTER II -

SOME REMARKS ON EC AND C.E.C. DETERMINATION.

A. GENERAL ANALYTICAL PROCESS.

The general scheme of investigating CEC and EC involves a three steps procedure:

FIRST STEP:

Absorbed cations are removed from exchange sites by a solution containing a saturating cation S (either S^{+} or S^{++}) and collected for subsequent determination. The leachate contains, in addition to original S ion, exchangeable Ca, Mg, Na, K and other minor exchangeable elements.

SECOND STEP:

The excess saturating solution which is held in the soil sample by capillarity is washed out and collected when necessary.

THIRD STEP:

The saturating ion S is displaced by a so called replacing solution containing a replacing cation R.

Notes:

- First and third steps are similarly done.
- During this sequence, exchange sites of soil are occupied successively by:
  - original exchangeable ions.
  - saturating cation S.
  - replacing cation R.

B. CHEMICAL FACTORS AFFECTING CATION EXCHANGE

a) Ionic charge

1. The higher the ionic charge of a cation, the stronger it will be fixed on a given exchanger. This general rule is true for soil, with few exceptions due to specific structure of some clays (illite, vermiculite..) or in acidic PH where exchange is low (WIKLANDER, 1974 cité par Ruellan, Deletang 1961).

2. A given ion-exchanger in contact with ions of different charges is more selective towards polyvalent ions in dilute solution and towards monovalent ions in concentrated solution.

Consequence:

It is therefore more convenient to use the combination S monovalent, R divalent rather than the contrary.

b) Nature of competing ions:

Among ions of similar charge, competition for occupying exchange sites depends on their mobility, i.e. their ionic radii, their hydration condition, and their atomic neight. (see table I):

- Table I -

Effect of ion nature on binding force on ideal exchange

ion*	ra**	re	n(H_2O)	A
Ag	1,26	2,5	-	108
Cs	1,00	2,5	-	133
Rb	1,48	2,5	0-1	85
K	1,33	3	4-6	39
HH4	1,43	2,5	2-5	-
Na	0.95	4	8-11	23
Li	0.68	6	10.14	7

* ions by increasing force of binding on Dowex 50 W (up to down) - Dow chemical company. ion-exchange.

ra = cristal ionic radius in Angstroms. (Lange's handbook of chem. Dean 1874).

re = effective ionic radius (Kielland 1937) used for calculation of ionic activities by Debye - Hückel formula.

n(H_2O)=number of hydradation molecules (average-values).

Note:

- The sequence for a montmorillonite-NH_4 would have been: Li - Na - H - K - Rb - Cs (Ruellan - Deletang).
- The H ion has a specific behavior. (GRIM 1953).

divalent ions:

For divalent ions, the increasing binding force on a soil, as a rough average: Mg - Ca - Sr - Ba.
(Montmorillonite - NH_4, muscovite-NH_4 and Kaolinite-NH_4, Rvellan Deletang 1967).

Consequence:

if S and R bear the same charge, R must lie on the right of S in any of the two list mentioned above.

c) Nature of pre-existing ion:

- The solution S has always to replace Ca, Mg, Na, K in varying quantities, but usually in this decreasing order. Being given four different pre-existing ions no simple rule can be used for choosing S.
- In the third step; if S is given, the increasing power of replacement of cation R is: (Jenny, Gieseking 1936).
  - if S is Ca: Li - Na - K - NH_4 - Al
  - if S is Ba: Li - Na - NH_4 - K - Ca - Al

d) Nature of the exchanger:

As already mentioned, some types of clay may fix, within their interlayer surface ions like NH_4, K, Rb and Cs. Such are, vermioullite, and Illite. The nature of clay may change the order of affinities:

for exemple: (from SCHACHTSCHABEL 1940)

on a Kaolinite-NH_4 order is: Li - Na - K - Ca (normal)

on a Muscovite-NH_4 order is: Ca - Li - Na - K - (Ca weakly bound).

e) PH of extracting solution:

For a given soil sample, the C.E.C found increases as PH to reach a maximum value between PH 8-9. This increase is due mainly to the organic fraction, and to much a lesser extend to the clay fraction. (C.E.C of organic matter may double from PH 4 to 8, while C.E.C of clay fraction may increase of 10% only. (Helling et al, 1964).

Consequence:

The ideal PH during EC extraction and C.E.C determination is the soil-PH. As changing the PH of solution for each sample is out of question, and usual values of 8,5, is arbitrary choosen for calcareous soils.

C. POSSIBLE SOURCES OF ANALYTICAL ERRORS

Apart from the usual relative imprecision of soil analysis the three steps procedure has inherent causes of errors.

a) ion competition
b) ion dissolution
c) ion hydrolysis
d) ion trapping.

a)- S may not fully saturate the soil, either because the selectivity of the soil for it is too low (if S is Li for instance) or because competing ions (Ca, Mg, Al) are brought into

solution during the first step. (from $CaCO_3$, dolomite, gypsum; ion competition may occur also in the washing step.

b)- Saturating solution may dissolve part of soluble Ca, Mg, Na or K, which are subsequently counted as exchangeable, leading to over estimated values of E.C. ion.

c)- When excess of S solution is washed out in the second step. Na and K may be removed by hydrolysis (or solvolysis).

d)- Na and K may be trapped between interlayers of vermiculite, illite and weathered micas. Under estimate values of ENa and EK would result in the first step, and underestimate value for C.E.C if Na or K has been used as saturating ion (Na acetate, K chloride).

D. LABORATORY TECHNIQUES:

As it is the use for all ion-exchange process two systems are possible:

- batch operation
- column leaching.

Complete saturation (step 1 or 3) is achieved in the first case by successive mixing and centrifuging.

In the second one a small quantity of displacing solution is added to the sample in a column, leached by gravity and the process is repeated as many times as required.

Leaching is a suitable technique for treating many samples at a time, but channeling and air trapping may lead to undersaturation. In the batch technique the sample is subject to strong mechanical treatment (alternative-shaker, ultra-sonic dispersion, centrifuging) which do not exist in natural conditions. Adoption of one or another system is mainly a matter of available equipment and number of sample to treat.

- CHAPTER III -

ANALYTICAL PROBLEMS AND THEIR SOLUTIONS.

Considering possible source of errors reviewed in CHAP. II, and the problems associated with the chemical composition of the sample we may classify the different methods into four classes:

- Nearly neutral soil samples.
- Calcareous or/and dolomitic samples.
- Saline or/and alkaline samples
- gypsyferous samples.

A summarized review of existing methods is given in each case with its range of application.

A. NEUTRAL OR ACIDIC SAMPLES

a) Difficulties:

No trouble is to be expected from neutral or acidic soils, except those containing high amounts of organic matter or high percentage of 2/1 type clay.

b) Solutions:

The widely spread Amonium acetate method (user by 50% of the labs. of developping countries. Brogan, FAO Soil Bulletin, 1965) consisted of the three steps.

- Saturation with $AcONH_4$
- washing with ethanol
- replacing by any convenient salt of Na, or K.

Among the short comings of $AcONH_4$ methods are: The non-exchange fixation of NH_4 on some clays, its weak exchange power and its likeliness to dissolve some organic matter if present in high amounts (OLLAT -COMBEAU PELLOUX).

As Ca and Mg extracted diminish as PH increase, when operating around PH 7 - 8, underestimates values are given. (OLLAT - COMBEAU).

Among the advantages: The naturally buffered PH 7 of amonium acetate, its easy volatilization, its negligible concentration in most soils.

Other methods include the use of $CaCl_2$ (OLLAT - COMBEAU, PELLOUX) or a mixture of $(ACO)_2Ba$ and $BaCl_2$ (DENIS-FREITAS, OKAZAKI, NIJENSHON) which eliminates the second washing step.

Appendix:

- Cf table N- I
- Cf methods N- II

B. CALCAREOUS OR DOLOMITIC SAMPLES:

I. CATION EXCHANGE CAPACITY OF CALCAREOUS SOILS

The solubility of calcium and magnesium carbonates (calcite, aragonite, dolomite) creates an additional difficulty. Ca and Mg brought into solution from the soil enter in competition with S ion in saturation step. A lower than real value of C.E.C is found. For this reason neither $ACONH_4$ or NaCl (Schmuck 1929) are convenient as saturating solution.

Three types of solution are proposed in the litterature:

a)- removal of carbonate prior to saturation.
b)- use of a reagent which doesnot dissolve Ca or Mg
c)- elimination of Ca ion competition.
d)- use of an ion non existing in the soil (Li, Sr...)

a) removal of carbonates prior to saturation:

1- removal by HCl or Acetic Acid may destroy clay fraction and alter true C.E.C.

2- ion-exchange removal of carbonates has been proposed, (ABDEL AAL - BERGSETH 1975). The method is suitable for carbonate content less than 10%

b) Among proposed non dissolving reagents:

1- ACONa (Bower)
2- $BaCl_2$ in TEA (MEHLICH).
3- NH_4Cl in ETOH (TUCKER).
4- a mixture of Amonium carbonate, Amonium Acetate and amonium oxalate. (PURI).

1) Sodium acetate dissolves less carbonates than amonium acetate and only few silicates are sufficiently extracted to lead to appreciable errors. But ion competion, and Na hydrolysis still occurs (POLEMIO RHOADES 1977).

2) $BaCl_2$ buffered (PH. 8,2) in triethanolamine is used by Mehlich (1942) as saturating solution concentration of Ba before and after saturation is taken as proportional to soil C.E.C Part of B_2 is adsorbed on $CaCO_3$ particles, part is precipitated as $BaCO_3$. Both these concentrations don't cuter into consideration when calculating C.E.C leading to inaccurate results, especially if a high specific surface of $CaCO_3$ or $MgCO_3$ induce important coating by barium ions.

3) NH_4Cl N, PH 8,5 in alcoholic solution is used by Tueker no washing step is required and NH_4Cl is displaced by KNO_3, $Ca(NO_3)_2$ replacing solution. The difference between NH_4 and Cl in the replacing leachate gives the C.E.C

   Chloride has to be absent in the soil, or removed by glycol-ethanol (solvent which does not encourage simultaneous ion-exchange).

   Limitations of this method are those associated with the noture of NH_4 already mentioned.

The second factor of the difference NH_4 - Cl is kept low by using N/10 or N/20 alcoholic NH_4Cl as final saturation step.

4) a mixture of amonium salts, as carbonate, acetate and oxalate, has been suggested and used to reduce the carbonate dissolution (by common anion effect of carbonate) and to precipitate calcium as soon as it enters into solution. This otherwise very elegant method suffers from the poor stability of the reagent.

C. Elimination of Ca competition:

1. The obvious way is to use Ca itself as saturating ion Ollat - COMBEAU propose a $CaCl_2$ N solution, followed by $CaCl_2$ N/10 for saturation step; and replacing by KNO_3 N, no washing step is necessary C.E.C is proportional to the difference $(Ca - (CO_3 + HCO_3 + Cl))$, dissolved Ca being counted as carbonate. It must be noted that if dissolved Ca does not alter the first step, it still compete with K in the third step.

d. Use of an ion non existing in soils:

1. If Lithium, is used as a mixture of chloride and acetate (Yaalon 1962) to sature the complex, no washing step is needed, for Cl is an index ion; replacing is done by $(ACO)_2Ca$, In this method, even low dissolution of Ca enhances ion-competition effect because of the low affinity of soils for lithium.

2. ^{90}Sr, ^{137}Cs, have been used; (AMAVIS 1959). These methods use the fact that when equilibrium is reached, the ratio radio active isotope/inert isotope concentration is the same in solution and in soil. The difference in radioactivity of the solution before and after equilibrium is directly related to C.E.C. However these methods require a complex equipment not comonly found in every laboratory.

II. Exchangeable cations of calcareous samples:

Neither Ca, Mg, Na or K may be used as S ion if they are to be determined as exchangeable cations in the same extract. Because of that the determination of EC in calcareous soils is more troublesome than CEC. Thus, solutions are more elaborated. There are two possibilities.

a)- Separate extraction of Na, K.
b)- Separate extraction of Ca and Mg.

a) Separate extraction of Na and K:

The simplest way is to extract Na and K by any suitable reagent (Amonium Acetate, calcium acetate, calcium chloride, among others). And to determine C.E.C separately. Exchangeable Ca and Mg are given by difference. Accuracy of this method relies on the assumption that all exchange sites are saturated, and on the reliability of the C.E.C value.

This system does not provide the individual ex. Mg concentration which may be of interest in some particular cases (magnesian toxicity, structural stability, alcalinization...) Further more, ex. Ca and Ex. Mg are overestimated if the soil. PH is less than 8,2, value under which there still remain some exchangeable H on exchange-sites (BRADFIELD 1933, DEMOLON 1952). In addition, it is a good practice to compare the sum of EC and C.E.C as a cross-cheeking of results.

Nevertheless, after having completed the first step of C.E.C determination, the leachate contain Ex.Na and Ex. K. (The dissolution of carbonate help in removing more quickly Na and K by ion-competition, allowing the use of a carbonate dissolving solution, at least for ENa and EK extraction).

b) Separate extraction of Ca and Mg

Whatever is the extractant used, a correction for dissolved carbonate is necessary. This correction is valid only for stricto sensu calcareous samples. No buffered saturating solution may be used.

1) extraction by NaCl (Hissink 1925). The sample is leached by two equal volumes of NaCl N. The first extracts Ex. Ca + Sol.Ca, the second extracts the same amount of Ex. Ca. The difference in Ca concentration of the two extracts represents Ex. Ca. It is supposed that all Ex. Ca is extracted by the first leachate, and that the dissolution of Ca-carbonate is proportional to volume of extracting solution.

2) On one NaCl extraction (TOUJAN 1960), Ca, HCO_3, SO_4 are determined and then:
Ex. Ca = Tot. Ca - (HCO_3 + CO_3 + SO_4)

3) NaCl and KCl seemed to be the most suitable reagent for using the correction method (PAPANICOLAOU, 1976) - NH_4Cl dissolving too much carbonates and LiCl having a low affinity for soil are not suitable.

C- SALINE AND ALKALINE SOILS

a) Introduction:

In arid zones, the frequent occurence of readily soluble salts, combined with more or less soluble non-wheathered minerals, like alkaline - earth carbonates creates additional difficulties. A permanent equilibrium exist between the soluble and the exchangeable cations. Therefore any change in total concentration of soluble salts, as it occurs when the moisture content of soil, or the soil/water ratio changes, induces a change in concentration(and possibly in composition) of adsorbed cations. These problems have been studied by numerous authors who propose only two possibilities to overcome these difficulties:

1- To perform extraction of exchangeable cations with any non hydrolysing solution, then to substract soluble cations in order to get only exchangeable ones. Soluble cations are determined in a separate extract. (Bower, Reitweier Fireman 1952, JACKSON 1958, NIZENSONN 1960, TOUJAN 1960).

2- The second possibility consist in leaching out soluble salts prior to the saturation-replacement steps. (Rich 1962, Tueker 1974). A solvent which does not encourage ion-exchange is used (methanol, ethanol, glycol...).

Both methods have the same limitations due to the same causes:

- There is no clearly defined boundary between what is soluble and what is exchangeable in a soil sample.
- The quantity of salts extracted, and counted for as "soluble" depends on:
  - The nature of the solvent used,
  - The soil/solvent ratio;

b) Methodology:

The first idea was to substract (Na + K) found in saturation extract from total (Na + K) found in the solution used for extracting exchangeable Na and K. Using the saturation extract to determine soluble salts is supported by two reasons: saturation percentage is practile moisture content closest to the field capacity. Secondly it exist a relation between soluble sodium expressed as sodium adsorpion ratio (SAR) and exchangeable sodium ratio (ENa/(C.E.C. - ENa). SAR is calculated from Na, Ca, Mg concentration in Sat. extract. A similar relation exist for K (GAPON 1933, Bower, Reitmeier 1954). For reasons already seen, one analysist can be lead to choose different saturating solution S for extracting exchangeable+"Soluble" cations. For instance, NH_4Cl, $AcONH_4$, AcONA, KCl, ACOK. The quantity of exchangeable ions extracted may be the same in each case, but the quantity of soluble ions extracted is probably different. The correction leads to different results.

For this reason many researchers have tried to eliminate soluble salts prior to the EC determination. Water cannot obviously be used and only non hydrolysing solvent are suitable. Unfortunately their ability to dissolve high quantity of salts is questionable.

A good combination of the two procedures is to wash out saturated extract by alcohol and then to carry on EC extractions.

D- Gypsiferous Soils -

I- INTRODUCTION:

The presence of gypsum, generally associated to alkaline - earth carbonates and alkaline soluble salts, adds another obstacle in the determination of EC and CEC. A great number of methods have been proposed, either for EC only of for the simultaneous evaluation of EC and CEC. All these methods have been subject to discussion, either because of their questionable reliability, or their complexity. Their review shows the diversity of the solutions proposed to evercome the low solubity of gypsum.

II- EXCHANGEABLE CATIONS

a) GEHRING (1929): Sodium sulfate saturation.

The soil is treated with an alcoholic solution of Na_2SO_4. Neither calcium carbonate nor gypsum are likely to dissolve in this solution.

- ECa is precipitated as calcium sulfate.
- CEC is proportional to the decrease in concentration from the original Na_2SO_4 solution.
- Excess of saturating solution is given by measure of weight before and after the saturation.

b) PURI (1936) - Saturation with barium carbonate

- The gypsum is changed into calcium carbonate by reaction with barium carbonate. The soil is saturated with barium. The sample is then treated as if strictly calcareous.

c) DURAND (1954). VANLANDE (1956). Constant dissolution of gypsum in NaCl solution.

- An excess of gypsum is added to all samples.
- NaCl is used as saturating solution and providing that two

successive extractions are similarly made, the quantity of gypsum dissolved in each step is the same. Thus the first extract contain ECa + Sol Ca, the second only Sol Ca ECa is given by the difference.

d) BOWER-REITEMEIER, FIREMAN 1951, TUCKER. LOVEDAY 1972-1974, DABIN 1975, MOLODSTOV 1975..

- Elimination of soluble salts.

Soluble salts are removed from the saturated paste.Soil is then sat.by an alcoholic solution of NH_4Cl which does not encourage hydrolysis - (desorption) of adsorbed Na and K and which does not dissolve gypsum in trouble some quantities.

Saturated paste may be avantageously replaced by a standard 1/1 extract which does not hydrolyse adsorbed Na-K and dissolve more soluble calcium than saturated extract (DABIN).

III) CATION EXCHANGE CAPACITY:

a) NIJENSOHN (1960): soluble Ca is precipitated as oxalate:
The soil if equilibrated with amonium oxalate. NH_4 saturate part of the exchange sites. (sol + Exh)Ca precipitates as calcium oxalate. Correction for Ca is done by measuring SO_4 and $CO_3H + CO_3$ in extracting solution. Cation exchange capacity is given by NH_4 extraction.

b) YAALON (1962): lithium is used in conjonction with chloride ions a saturating ion.
Lithium acetate may saturate the complex, despite the low affinity of soil exchange sites for lithium; the method omitting the washing step to avoid desorption, and using Cl as index for the lithium retention suitable if chloride is present in soils, which is frequent, not to say always the case in gypsic samples lithium is replaced easily by calcium from a $(ACO)_2Ca$ solution.

c) BASCOMB (1964): gypsum is transformed in $BaSO_4$:
A great excess of $BaCl_2$ N PH 8,1 is added to the soil. The sulfate anion is precipitated as $BaSO_4$. The calcium cation passes into solution as $CaCl_2$. No more gypsum remain in the soil and the excess of barium may saturate the exchange complex.

d) TUCKER LOVEDAY (1974) use of a reagent which does not dissolve gypsum
- Saturation is done by NH_4 ion in alcoholic medium after having eliminated soluble salts by a mixture of glycol-ethanol.
Replacing solution is a mixture of KNO_3 and $Ca(NO_3)_2$.
Washing is done by an alcohokic solution of NH_4Cl N/20.
Technical difficulties appears for some soils it clay disperse during the washing step.

e) GARMAN-HESSE (1975) coating of gypsum partials
propose an excess of $BaCl_2$ as saturating solution gypsum is coated with insoluble $BaSO_4$ and does not interfere during the saturation step.
Replacing solution is $MgSO_4$ (N/20) - CEC is proportional to the decrease of Mg concentration; the authors found calcium dissolved in the second reagent which is likely to destroy the protective coating formed during the first step.

f) OLLAT - COMBEAU (19)
- correction for dissolved gypsum
- $CaCl_2$ in PH 7,0 is used as saturating solution. Washing is done by $CaCl_2$ N/10.
- Extraction of adsorbed Ca is done by KNO_3N (OLLAT-COMBEAU) or $NaNO_3$ PH 7,0.
CEC is given either by tot. Ca - ($Cl + CO_3 + HCO_3 + SO_4$) or by tot. (Ca + Mg) - ($Cl + CO_3 + HCO_3 + SO_4$) if the soil contain

soluble magnesium carbonates. The precision of the method is lowered by the numerous required analyses.

g) POLEMIO-RHOADES (1977). Two steps procedure
In this method, saturation is done by (ACONa 0,4N NaCl 0,1N in ETOH 60%) - No washing step is required and replacing of fixed Na is done by $MgNO_3$ PH 7,0,Na andCl are determined in the last solution.

The value found for Cl serves as correction for the excess of saturating solution held by capillarity in the first step.

IV- Note:

Discusion on methods for gypsic samples: a) on gypsum dissolution:

The speed of dissolution of gypsum in a sample depdns, for the same solvent, on the size, the shape, the specific surface, the more readily will be dissolved. This leads to two remarks.
- method assessing a low dissolution for gypsum in a given extractant are suitable only if a parallel way of checking how much gypsum has been dissolved exist (by SO_4 determination for instance).

b) on elimination of soluble salts:
The removal of soluble salts is subject to limitations already discussed. This removal is practical only under certain conditions in each methods.
- if chloride is less than 0.1% in Tucker's method.
- if EC of saturated extract is less than 2 mmhos/cm in Rhoades' method.

- on method by difference:
methods measuring the adsorption of a given cation by loss of concentration of the saturating solution (Gehriny, Garman. Hesse) are not precise but suit particularly when matrix effects are important in the determination. (flame emission - absorption for instance), the difference eliminating the effect of possible interferences.

- <u>on lithium cation</u>

ion competition is particularly defavourable to lithium even if few Ca is present in solution (Raponicolaou, Rhoades).

- CHAPTER IV -
- DETAILED METHODS -

CONTENTS:

Methods

Method	saturations solution	washing	replacing solution	Analytical determination (CEC only)	Results	Range of application	Restrictive factors
(1)	ACONH4 1,N,PH7	ETOH 95°	a)none b)KCl N	a)NH4 by direct distillation b)NH4 in KCl solution	EC/CEC	Neutral Soils only	-organic metter -illites-vermiculites - micas. (2/1 type clays)
(2)	CaC12 1.0N PH7	CaC12 N/10	KNO3 N	Ca, Cl	EC/CEC (except ECa)	Neutral, slightly calcareous soils	-soils with low CEC
(3)	(ACO)2Ba 0.4M + BaC12 0.1M	none	ACONH4 N	two for Ba, two for Cl	EC/CEC	Neutral soils	
(4)	(ACO)2 Ba	none	none	Barium only	EC/CEC	Neutral soils	remark:method by difference
(5)	BaC12 0.2N TEA PH 8.1	water	a)none b)NH4C1 N	a)Ba by direct titration b)gravimetric	EC/CEC	neutral soils	method a)particularly rapid for routine tests
(6)	BaC12 0.2N TEA PH 8.1	water	none	Ba1,Ba2,in two successive extractions	E(Ca+ Mg)ENa, EK CEC	calcareous soils	remark:many determinations to be carried out.
(7)	NH4C1 N ETOH 95° PH 8.5	no	CANO3, KNO3 (0,2N,2N)	NH4, Cl	EC/CEC	calcareous slightly gypsic soils	remark:pretreatment to wash out soluble salts.
(8)	ACONa N	ETOH 95°	NH4OAC N	Na	ECa,EK, EMg,CEC	calcareous (saline alkaline)	usable for saline samples if soluble salts are eliminated
(9)	ACONa NaCl	no	MgNO3 N	Na, Cl,	E CEC	calcareous gypsiferous	
(10)	ACOLi LiCl	no	(ACO)2 Ca	Li, Cl	EC/CEC	neutral soils	

- Method 1 -
(EC/CEC neutral soils)

- Saturation:
  - 4-7 gr (po) of soil are shaken 15 min. with 50 ml of $ACON_4$,N PH 7,0, then soil + solution are left overnight.
  - the solution is filtered and the soil is leached with fractions of 25 - 30 ml until about 240 ml (or V ml) are collected in a 250 ml flask. Volume is made to 250 ml with saturating acetate solution.
  - Exchangeable cations are determined in this solution.

- washing:
  - the soil is leached with 95^0 ethanol until no more amonia is detected by Nessler's reagent in the washing. Excessive washing is to be avoided.

- replacing:
  - the adsorbed NH_4 is replaced by K from successive washings by 30 ml portions of KCl N PH 7.0 replacing solution.
  - leachates are collected in a 500 ml flask (or V2 ml) NH_4 is measured by indo-phenol absorption or by distillation.

- direct distillation:
  - to avoid replacing step, transfer the washed soils directly in a Kjeldhal flask (800 ml)
  - add slowly 25 ml of 25% NaOH, avoiding mixing of solutions.
  - Carry out distillation in a convenient apparatus. Amonia is collected in about 25 ml of 2% boric acid in which few drops of indicator A has been added. Titrate with H_2SO_4 N/10
  - Carry out a blank (4-7 gr pure silica) in the same conditions. each ml of H_2SO_4 is equivalent to 1,4008 mg of N, or to a CEC equal to10/po(meq/100 gr) of soil.

Notes: CEC is slightly underestimated, in comparison with ACONa method.
  - NH_4 may be strongly fixed on 2/1 clays, giving a low value for CEC.

Reference: Bower, Reitemeier, Fireman (1952), Bower 1955 Pratt, Holoway-chuck (1954); Renjifo (1974).

- Mehtod 2 -

(EC/CEC neutral and slightly calcareous soils)

- Saturation:

  Place p, (f.i:4-6 gr), in a 50-100 ml centrifuge tube, add 30ml of $CaCl_2$ N PH 7,0 saturating solution. Shake 15 min. centrifuge. Repeat three more times.

  - collect supernatant and adjust to 100 ml for EC determinations.

- washing:

  wash by $CaCL_2$ N/10 (Ollat-Combeau) or $CaCl_2$ N/20 (Papanicolaou).

- replacement:

  - Mix the soil with 30ml KNO_3 N PH 7,0 replacing solution, shake, centrifuge. Repeat six to eight times and adjust to final volume 200-250 ml (f.i V ml)
  - titrate Ca, Mg, Cl, CO_3, HCO_3 in this solution. If results are expressed in meq/l, then: $CEC = ((Ca+Mg)-(Cl+HCO_3))/10.V.po$ (po = weight of soil sample calculated on an oven.dry basis).

- note: ECA and EMg may be extracted separately with KNO_3. The method is suitable for column operation with increased volumes of saturation (250 ml) and replacing solution (500 ml)

- Titration of Cl

  - To 50 ml of leachate add 5 ml of HNO_3 50% .
  - excactly 10 ml $AgNO_3$ N/20 with a precision pipette.
  - about 3 ml of nitrobenzene, or sulfuric ether
  - 1 ml of saturated amonium-iron sulfate solution. Mix during one minute to coagulate AgCl precipitate, titrate excess Ag by KSCN N/20 until orange colour appears (this colour must be stable for at least one minute).

References:

- Ollat - Combeau, 1960
- Papanicolaou 1976
- Pelloux 1971.

- Method 3 -
(EC/CEC neutral soils)

saturation:

- place p gr (4 to 6 gr) of sample in a 40ml centrifuge tube; weigh tube + sample: wo gr.
- add 20ml saturating solution $(ACO)_2Ba$ 0.4M + $BaCl_2$ 0.1M, shake 20 min. centrifuge. Collect supernatant if EC are requested; repeat wahing for a total of six washes; weigh tube + soil + excess saturing solution: w1 gr.

Replacement:

- add 20ml $ACONH_4N$, shake 20 minutes - centrifuge
- repeat to a total of eight washes. Collect supernatant make combined extracts to 200ml (or V ml) with replacing solution. Be this solution I.

Calibration: weigh a known amount of 0.4M $(ACO)_2Ba$+0.1M $BaCl_2$ solution (f.i:x grams) make up to V ml with $ACONH_4$ 1N. Be this solution II.

Calculation:

1) take a v ml aliquot (10ml) of each solution I and II, acidify, titrate with 0.005M $Hg(NO_3)_2$ using reagent C. Be ClI and ClII, chloride concentrations expressed as meq/l.
2) take a v1 ml aliquot (10ml) of each solution I and II, add b ml (1 to 3 ml) of 1% $SrCl_2$ solution. dilute to v2 ml. (50ml). Determine Ba in each aliquot. Be Ba1 and Ba2 concentrations exp. as meq/l.

Results: CEC = f (tot. Barium - excess Barium)

total Ba (Meq/100 gr) = C1.v2.V/v1.10.p

excess Ba (Meq/100 gr) = 10.C1 (w1-w0)/x

alternative: excess Ba (meq/100 gr) 10 C2.(ClI/ClII)

Note: the quantity x must be choosen approximatively as p/4 if centrifuge is used and P/2 if leaching is preffered.

- the standard errors of this method are important.

References: - Mehlich 1948 - OKAZAKI 1964 - SMITH et al. 1966 - Giltrap 1972.

- Method 4 -
(EC/CEC neutral soils)

Saturation:

- weigh p gr of soil (1-2 gr.) add the same amount of pure, acid washed silica sand. Transfer in a funnel or column.
- Leach with 90 ml of 0.0375M $(ACO)_2Ba$. Collect leachate in a Vo ml volumetric flask (100ml) Make up to the mark with original saturating solution. (solution I).
  a) pipette a v1ml aliquot (15ml) add 5ml of urea-dichromate reagent D. Boil until the supernatant is clear. Filter, wash, make filtrate+washing to v2ml (50ml).
  b) pipette a v3ml aliquot (10ml) add b ml of Sr 2% releasing agent, determine Ba in this solution.
  c) if necessary take part of solution I for EC determinations.

Calculation:

CEC (meq/100 gr)=(Co-C)(v3+b)(v2.v0)/v3.v1.10 p.

C and Co being Ba concentration (meq/l) in a v3 ml aliquot of solution I and in a blank done under similar conditions.

Notes:

- Values obtained are comparable to $(ACO)_2Ca$ method. (Giltrap).
- reproductibility is inferior to conventional $ACONH_4$ method.

References:

Giltrap 1972

- Method 5 -
(EC/CEC Neutral Soils)

Saturation:

- Place p grams (4 to 6) in a büchner funnel on a filter paper disk. leach with 25ml 0.2N $BaCl_2$ TEA PH 8.1, and then by 25ml 0.2N $BaCl_2$ without TEA.

washing:

- With 50ml of dist water. leachate and washing are collected, made up to volume V ml (100-150ml) and exchangeable cations are measured.

1) First possibility

Replacement: Ba-saturated soil is titrated by standard $MgSO_4$ solution. $BaSO_4$ precipitates and the end of titration is shown by an abrupt change in the conductivity due to the high specific. ionic conductance of free SO_4 ions.

2) Second possibility

Fixed Ba is replaced by NH_4 from successive equilibrium from a NH_4Cl N solution. (up to 250ml), leachate is labelled solution B. (be it V ml)

- A V ml aliquot of B solution (50ml) is diluted twice and 1,5ml 5N HCl is added to acidify.
- 1 gr sulfamic acid is added and the solution is heated to 60-70° in a water-bath, 30 minutes after the first turbidity appears. Filter, wash with hot water, dry, iguite at 800° weigh.

If m (milligrams) is the weight of the precipitate: CEC meq/10 gr.= 4,276m x V/p.v1

Note:

Methods by difference using Ba ion are not applicable to soil containing $CaCO_3$ or $CaSO_4$, $2H_2O$ - (loss of Ba adsorbed on around these particles being not taken into account.)

- Method 6 -

(EC/CEC calcareous soils)

first saturation:

- Place p gr (5gr) of soil in equilibrium with p gr of water during 24 hours.
- Transfer to a percolation tube and add 25ml 0,2N $BaCl_2$,TEA, PH 8.1
- leach 25 ml 0.1N $BaCl_2$ alone.

washing: wash the soil with 25ml of dist water, freshly boiled collect all the leachates in a V ml volumetric flesk (100ml) label it extract A. This extract contains soluble and exchangeable cations.

Second saturation:

- A second extraction is carried out with the same reagents (25ml Ba, TEA 0,2N; 25ml Ba, 0.1N; 25ml H_2O) label it extract B. This extract contains soluble cations only. A blank is done with pure silica sand (having a particle size distribution comparable to a soil)for both extracts A and B.

Calculations: The difference in Ba concentration in the first extract between sample and blank represent the CEC versus Ba. (It is therefore important to leach exactly the same quantity of $BaCl_2$ solution for all samples and blank)

- Exchangeable cations are measured as being the difference of their concentration in the first and the second extract.
- For exchangeable Ca and Mg, a correction is necessary for dissolved carbonates, expressed as the sum (CO_3H+CO_3) in both extracts.

Note:

1) Since solubilities of Mg carbonates and Ca carbonates are different, it is not possible to separate ECa from EMg. Furthermore, it is not safe to assume that the quantity of salts dissolved in the first and the second extract is the same in two cases:-

- if the soil contain few soluble salts (all of them could be found in the first extract, making correction impossible)
- if the soil contain high quantity of soluble salts (the more readily soluble salts passing into solution in the first extract, the quantity shall be relatively higher than in the second one). It is therefore a good practice to grind the soil sample, to 0,1 mm . Such grinding eliminating the surface effect.*

2) Ba being strongly fixed on exchange sites, washing does not produce noticeable hydrolysis. - CARPENA: - MEHLICH: 1945.

* with a preliminary grinding, there is a risk of modification of natural exchange properties.

- Method 7 -

(EC/CEC calcareous, slightly gypsiferous samples)

Pretreatment:

1) if soluble chlorides lies in the 0-0.1% range.
   - Mix 2 gr of soil with 25ml 10% Ethylene glycol alcoholic solution
   Shake 30 min. centrifuge.

2) repeat the process if soluble chlorides exceed 0.1%.

Saturation:

- add 20ml alcoholic NH_4Cl PH 8,5, agitate. 30 min. centrifuge.

Repeat the process three more times. The last saturation is done by N/20 Alcoholic NH_4Cl. Collect supernatants in a v,ml flask (100ml) add few drop conc. HCl to acidity, make up to volume with saturating sol. Measure exchangeable cations in this solution.

Replacement:

To the NH_4 saturated sample add 25ml ($CaNO_3$, 02N; KNO_3 2N) shake 30 min, centrifuge. Repeat two more times and collect supernatant in a v2 ml volumetric flask. (100ml)

- determine on this solution NH_4 (meq/l) and Cl (meq/l).

Calculation:

$$CEC = (NH_4 - Cl) \times v2/10\ p$$

Note:

the same method might be used in a column using leaching instead of centrifuging.

Reference:

Tucker j. of soil science 3,25, 1974.

- Method 8 -

Classic amonium acetate method.

saturation:

p.gram (4 to 6) of sample are Shaken with 30ml N ACONa, PH8,2. during 5-10 min. centrifuge, collect supernatant if necessary for EC, redisperse. Repeat two more times. label this extract A.

washing:

- by 30ml portions of 95% Ethanol. The electric conductivity of the last washing should be less than 40 micromhos. cm^{-1}, further washing must be avoided.

replacement:

replacement is done by three 30ml N $ACONH_4$ portions, mixed with soil, then centrifuged, and collected in a V ml flask (100-150ml) made up to volume by the necessary quantity of replacing solution. This is solution B.

Coloulation:

Na is measured by AAS or Flame emission after convenient dilution. If Na is the concentration in solution B expressed as meq/l, then:
CEC (meq/100 gr.) = Na.v/10p.

Notes:

a) If reagents are made in 50% acetone, instead of water, a slightly higher value is found for CEC (Sayegh 1978).
b) Method is precise and widely used for slightly alkaline soils. (it could be necessary to increase the volume of saturating solution to eliminate soluble sodium salts)
c) Ethanol may be replaced by methanol or isopropanol.
d) Exchangeable cations may be determined in extract A after convenient correction for dissolved carbonates and dissolved sulfates. (Gypsum).

$$ECa = tot.\ Ca - (CO_3H + SO_4).$$

e) This method is usable when samples contain appreciable amounts of soluble salts. The modification are the following :-

1. a saturated extract is made separetely and "soluble salts" are determined in it. Values found are substracted from ECa, EMg, EK. Exchangeable sodium is determined separately (with $ACONH_4$ for instance). (Bower).

2. "soluble salts" are measured in a systematic 1/1 extract. (Dabin). Substraction is made as in Bower's method.

3. Soil is saturated with water, saturating water is then extracted by a centrifuge. Excess water is expelled from the soil by treatment with 70% ETOH until elimination of soluble salts (lead nitrate test for SO_4, $AgNO_3$ test for Cl.) then EC are extracted with 0.1N NH_4Cl in 70% ETOH (Molodstov. Isnatova - 1976. See also Tucker - Loveday 1974).

   This treatment doesn't eliminate SO_4 which has a low solubility in alcoholic solutions.

References:

- Bower, Reitemeier, Fireman, Soil, Science 73, 19
- Jakson, Soil chemical analysice, Prentice Hall, 1958
- Pelloux, Dabin, Exchangeable cations and cation exchange capacity. ORSTOM 1971.

- Method 9 -
(CEC, gypsiferous soils)

Saturation:

p grams of soil (2m/m) are shaken with 33 ml 0,4N ACONa, 0.1 N NaCl Alcoholic solution. The process is repeated three more times.

Replacing:

Na saturated sample is extracted with three 33 ml increments by in PH 7,0 $MgNO_3$. Collected extracts are made up to known volume Vo ml (i.e. 100ml). Both sodium (tot. Na) and chloride (tot. Cl) are measured as meq/l in extracting solution.

Calculation:

$$CEC = (Nat - (Cl\ (C_1 + C_2))/C_2)\ Vo/10p$$

where $(C_1 + C_2)/C_2$ is the factor for determining the remaining saturating solution, held by capillarity after the saturation step.
C_1 being he exact Na concentration ACONa, and PC_2 being he exact Na concentration of NaCl, in the saturating solution.

Reference:

Polemio Rhoades, SSSAJ 41, 3, 1977.

- Method 10 -

Saturation with Lithium

Saturation

- 456 gr of soil (2m/m) are mixed with 20ml portions of 0.5N ACOLi, 0.4N LiCl saturating solution, strongly agitated, then centrifuged. Supernatant are collected until 200ml. (8-90 extractions).

Replacing:

by successive extractions of fixed Li by 0,2N $(ACO)_2Ca$ solution. Extractions are carried out by mixing-shaking-centrifuging - all extracts are collected in a 200ml volumetric flask; (solution B).

a) Lithium is measured in the calcium acetate extract after convenient dilution.

b) chloride is titrated in an aliquot of the calcium acetate replacing solution: 20ml of B solution are transferred in a Erlenmeyer flask. Add 20ml dist. H_2O and 0,5ml conc. nitric acid. Add few drops of diphenyl carbozone reagent (reagent B) titrate with mercuric nitrate N/50 until permanent violet-pink color.
: Substract value found for a blank. made on the $(ACO)_2Ca$ original solution.

Calculation: calculate CEC as being proportional to the difference: (Li - fCl) where: f=Li sat/Cl sat Li sat = exact Li concentration in saturating solution. Cl sat = exact Cl concentration in saturating solution.

Note: There is a strong competition between Ca and Li ions in calcareous soils, this leads to two remarks.

1. leaching through column cannot be used.
2. Li doesnot replace fully adsorbed cations in calcareous-gypsiferous soil samples, even after numerous equilibrium, because the ion-competition taken place during each leaching (Papanicolaou)

- The method is not usable if the soil contain soluble chloride. (except if chloride are washed out prior to saturation).

References:

- Yaalon:
- Dewis-Freitas.

- Method 11 - (outline)
(CEC gypsiferous soils)

Saturation:

Soil is saturated by a large excess of IN $CaCl_2$ PH8.1

washing:

a saturated $MgSO_4$ solution is used to replace adsorbed Ca.

calculation:

CEC is proportional to the difference of Mg concentration in the deplacing solution before and after Ca desorbtion.

Notes:

$MgSO_4$ solution being acidic, carbonates are readly soluble in it the protection with $CaSO_4$ coating around gypsum particles being not resistant to $MgSO_4$ treatment (Garman-Hesse). Therefore Mg must be measured by a method free from Ca interferences.

References:

Baccomis J.Sc. food and Agriculture 1964 vol.15.

Garman-Hesse. Plant and Soil 42, 1975.

- Method 12- (outline)
(CEC gypsic and calcareous samples)

Pretreatment:

The soil is shaken with oxalic acid, 1N during 1 day. gypsum precipitates as insoluble $(C_2O_4)_2Ca$. CEC is then measured by the conventional method.

Alternative:

The soil is shaken with amonium oxalate IN, calcium brought into solution from gypsum precipitates as Ca oxalate and soil is saturated by NH_4. CEC is measured by direct NH_4 distillation.

Note:

This method gives a higher CEC value (30 - 50% higher) than amonium acetate method, when applied to calcareous, gypsiferous soils (Sayegh 1978).

References:

NIJENSOHN.

PREPARATION OF REAGENTS

method N° 1: (Bower Reitmeier. Fireman)

Reagent A: (method 1) 0.2 gr bromocresol green + 0,1 gr methyl red dissolved in 100ml 95% Ethanol.
colour: acid: wine red; neutral blue-grey (PH 5,1) alcaline - green.

Reagent A': (Substitute for A, method 1)
1 part of methyl red 0.2% in ETOH 95° + 1 part methylene blue 0.1% in ETOH 95° (colour from violet to green).

$ACONH_4$ N, PH 7,0: for each liter of solution: 50ml ACOOH + 75ml conc. amonia (d 0,91 - 0,92 or 25 - 27% NH_3) adjust PH to 7,0 by ACOOH or NH_4OH if necessary (pH = 1/2 (pKa + pKa) = (4,75 + 9,25)/2 = 7,0

method N° 2: Prepare for each liter of solutions

A. Triethanolamine 15ml
HNO_3 (d = 1,33) 5ml
adjust to 500ml (about)

B. $CaCl_2$, $2H_2O$ = 73,5 gr.

mix A and B just before analysis. Adjust to PH7 either by HNO_3 or TEA.

Reagent B:
methyl orange 0.1 gr in dist. water(change of colour from orange ro red).

$CaCl_2$ N/10: 7,35 gr of $CaCl_2$, $2H_2O$ for 1l.

KNO_3 N : from KNO_3 101 gr/l. (slight heating improve speed of dissolution).

KSCN N/20 : 4,8590 gr KSCN prealably dried 105°C. Complete to 1000ml with dist. water. Check with standard $AgNO_3$.

Method 3:

Reagent C:bromophenol-blue: 0.05% in ETOH 95^{0}
diphenyl carbazone: 0.5% in ETOH 95^{0}

Method 4:

Reagent D:Urea-dichromate reagent:
0,05M $(NH_4)_2\ Cr_2O_7$ in 0,125M urea and 0,15M acetic acid.
0,0375M $(ACO)_2Ba$: 9,57 gr. $(CH_3CO_2)_2Ba$ in one liter freshly prepared dist. water. well closed.

Method 5:

0.2N $BaCl_2$, TEA PH0.1: solution A: 24,4 gr $BaCl_2$, $2H_2O$/1, solution B: 7ml TEA (7,5-8,0N), diluted to 30-50ml, add 24ml HCl N. Mix A and B. adjust PH with TEA in or HCl N

NH_4Cl N solution:53,5 gr NH_4Cl add 10ml amonia 10%, for 1l check PH PH8,0 adjust if necessary.

Method 6:

0.2N $BaCl_2$, TEA, PH0,1: as above

0,1N $BaCl_2$: 12,2 gr of barium chloride, dihydrate, diluted to 1l with dist. water.

Method 7:

Ethylene glycol/Ethanol solution: Mix 100ml 1,2 ethanediol (ethyleneglycol) with 900ml 96^{0} ETOH. Pass slowly through a column of mixed but ion vesin to deprotonize. Discard the first column volume.

N alcoholic NH_4Cl: dissolve 54 gr of NH_4Cl in 240ml water. add 670ml of high-grade ETOH. Add enough 25% amonia to bring the PH to 8,5

0.2N $CaNO_3$; on KNO_3: Dissolve first 150 gr of KNO_3 in hot water, then dissolve 60gr $Ca(NO_3)_2$, $4H_2O$ and make up to one liter

Method 8:

N.ACONa: a) from 136,1 gr/l CH_3COONa, $3H_2O$
b) from 82,04 gr/l CH_3COONa.

N $AlONH_4$: cf method 1.

Method 9:

0.4N ACONa, 0.1N NaCl, ethanol 60%

54,5 gr ACONa, $3H_2O$ dissolved in 240ml dist. water. Dissolve 5,8 gr NaCl and complete to one liter with 96^{O} ethanol.

N $MgNO_3$: dissolve 128,20 gr $Mg(NO_3)_2$, $6H_2O$: (1000 ml, freshly boiled water.

Method 10:

0.1N ACOLi, 0.4N LiCl: 17,0 gr of anh. LiCl dissolved in 20ml of water under cooling. Dilute to 60ml about, add 10,2 gr ACOLi, $2H_2O$ dissolve, adjust PH to 8,2 by LIOH 0,1N or to PH 7,0 by acetic acid. Adjust to 1l. The exact Li and Cl concentration is determined by conventional methods.

0.2N $(ACO)_2Ca$

1) Prepare 2 litres, 1N calcium acetate from 1l 2N acetic acid in which you add 1l of $Ca(OH)_2$ 2N freshly prepared (i.e. 74gr/l $Ca(on)_2$ and 66ml about of 80% zetic acid.

- CHAPTER V -

NUMERICAL DATA

A. FACTORS INFLUENCING CEC
   - Physical composition.
   - Size of particles.
   - PH of soil.

B. CROSS-CHECKING OF ANALYTICAL RESULTS.

C. TABLES.

A. FACTORS INFLUENCING CEC

a. Physical composition:

If x_1 and x_2 are the percentage of organic watter and clay respectively, CEC can be expressed as:

$CEC = ax. + bx_2 + e$

a being usually higher than b. This relation is valid for a given type of soil, in a limited area. No such a relation could be used by the analyst to check experimental CEC vlaues of samples from different origins.

For information, some value of b factor (meq/100 gr of clay):

- clay	b
1/1 Kaolinites	10
2/1 illites	20-40
2/1 vermiculites	100-150
2/1 Montmorillonites	50-150
3zeolithes	100-300

(from caillere - Henin - miner logie des argiles)

These numbers are rough estimate, as numerous specific factors must be considered independantly. Furthermore, silts and very fine sands have a meesurable exchange capacity.

b. Size of particles:

For a given sample, the finer the particles, the higher the CEC. An important analytical consequence is the use of standard preparation of sample (through 2 m/m sieve). Finer crushing to eliminate more easily soluble salts is to be avoided. (particularly for Kaolinites and vermiculites). The effect of crushing is to enhance all properties proportional to specific surface (CEC among others) for exemple, for a gypsic soil increase of CEC may reach 25% from 2m/m to 0.15 m/m and 35% from 65% 2m/m. (Sayegh 1974) for the same treatment.

c. PH:

Variation of CEC with PH has been extensively studied. The choosen value 8-9 for the PH of extracting solution corresponds to an alkalinity which gives maximum values. When using PH7 it could be expected to find values 5 to 20% less than when operating at PH 8.2. (Pratt 1961).

B. CROSS CHECKING OF ANALYTICAL RESULTS

a. It has been shown (US salinity lab 1954) that the equilibrium between soluble and adsorbed Na is expressed under mathematical form:

$y = 0.01475x - 0.0126$ $(r^2 = 0.852)$

where y is the exchangeable sodium ratio: $y = ENa/(CEC-ENa)$

and x is the sodium-adsorption ratio $x = (Sol\ Na)/(Ca + Mg)^{1/2}$

$x = Na/((Ca + Mg)/2)^{1/2}$.

b. more recently (Kittrick 1976) a study has been made on soils of arid zones having a saturated extract ionic concentration from 3,8 to 988 meq^{-1} and a sodium saturation percentage from 0.6 to 80%:

the relation: $\lg \frac{ENa}{ECa} = 0.79 \text{ kg } \frac{aNa}{aCa} - 1,41$ $r = 0.98$ has been proposed.

(ENa representing Exchangeable sodium, and ANa, the activity of sodium ions in saturated extract).

The usefulness of this relation being limited by the use of activities which are directly available, except if a selective electrode has been used for determination in the saturated extract.

c. Another relation is given (FERNANDO 1977) which relies dielectric dispersion of a soil-solution to CEC.

- C TABLES -

* Solubility of NaCl in $MgCl_2$ solution (25^oC,% weight)

Table I

$MgCl_2$ concentration: (% weight)	0	4,5 N	5	10	15	20	25	30
NaCl solubility (% weight)	26,4	20,6	20,5	15,2	10,5	6,5	3,3	1,1

in a N $MgCl_2$ solution, solubility of NaCl is 20,6% weight, i.e. approx. 300 millieq. for 100ml $MgCl_2$ solution. Thus $MgCl_2$ cannot be used as extractant for ENa in saline and alkaline soils.

Table.II

Solubility of some salts (given in grof solute for 100 gr water solution, 20^oC).

K_2CO_3	52,6	$MgSO_4$	25,2
$NaNO_3$	46,7	Na_2CO_3	17,9
$CaCl_2$	42,7	Na_2SO_4	16,1
$MgCl_2$	41	K_2SO_4	10,0
NaCl	26,4	$NaHCO_3$	8,7
KCl	25,6	$CaSO_4,2H_2O$	0,23
$KHCO_3$	25,2	$CaCO_3$	0,006 ($PCO_2=32x10^{-5}$atm)

from: International source book on irrigation and drainage of arid lands (FAO/UNESCO 1976.) p 185.

TABLE 3

properties of index ions used in CEC and EC determinations

	a	b	n
<u>divalent:</u>			
Ba	1,35	5	-
Sr	1,13	5	
Ca	0,99	6	
Zn	0,74	6	-
Mg	0,65	8	-
<u>monovalent:</u>			
Cs	1,0	2,5	2
K	1,33	3	3,5
NH_4		2,5	3,5
Na	0,95	4	8
(H)	(2,00)	(9)	
Li	0,60	6	12

a : ionic radius in cristalline state. (A^0)

b : effective ionic radius (Kielland 1937)

n : approx. number of hydratation molecules. (calculated as an average, values varying among different authors. From Ruellan-Deletang) ions are classified in the decreasing order of their binding force to Dowex 50w synthetic ion exchanger. (From Ion Exchange, Dowex, Dow chemical Company).

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CHAPTER IV

Detailed Methods

CHAPTER V

Numerical data.